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Received 16th January 2007, Accepted 3rd May 2007
First published as an Advance Article on the web 24th May 2007
DOI: 10.1039/b700719a

Depleted uranium (DU) weapons testing programmes have been conducted at two locations within the UK. An investigation was therefore carried out to assess the extent of any environmental contamination arising from these test programmes using both alpha spectrometry and mass spectrometry techniques. Uranium isotopic signatures indicative of DU contamination were observed in soil, plant and earthworm samples collected in the immediate vicinity of test firing points and targets, but contamination was found to be localised to these areas. This paper demonstrates the superiority of the ^{235}U : ^{238}U ratio over the ^{234}U : ^{238}U ratio for identifying and quantifying DU contamination in environmental samples, and also describes the respective circumstances under which alpha spectrometry or mass spectrometry may be the more appropriate analytical tool.

Introduction

Natural uranium (U) principally consists of three isotopes, primordial ^{238}U ($t_{1/2} = 4.47 \times 10^9$ y) and ^{235}U ($t_{1/2} = 7.04 \times 10^8$ y), which are parent members of a natural radioactive decay series, and ^{234}U ($t_{1/2} = 2.45 \times 10^5$ years), which is a member of the ^{238}U decay chain. For natural U, the ^{235}U : ^{238}U activity ratio has a constant value 0.046 (Table 1), while the ^{234}U : ^{238}U activity ratio is variable as a consequence of decay chain disequilibrium that arises from preferential transfer of ^{234}U to surface and groundwater.[1,2] This disequilibrium results in pronounced ^{234}U : ^{238}U activity ratio variations, but for soils the commonly observed range is 0.8–1.2 (*e.g.* ref. 3 and 4). Depleted uranium (DU) is a byproduct of U enrichment processes, whereby the fissile isotope ^{235}U is preferentially concentrated for the production of nuclear fuel or nuclear weapons. The enrichment processes, *e.g.* gas centrifugation or gaseous diffusion, also separate ^{234}U from ^{238}U, leaving a waste material (DU) which is depleted with respect to both ^{234}U and ^{235}U. Although the exact isotopic composition of DU, particularly that used by the British military, has been determined on relatively few occasions,[5,6] and thus may exhibit some subtle variation, DU has an isotopic signature strikingly distinct from naturally occurring U (Table 1). This isotopic difference can be used to identify and quantify contamination in the environment arising from the use of DU munitions, with both the ^{234}U : ^{238}U and ^{235}U : ^{238}U ratios being potentially useful for this purpose.

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Due to its high density (19.05 g cm^{-3}), penetrating power, and pyrophoric properties, DU has been used for military purposes such as tank-piercing ammunition and tank armour. In the UK alone, research and development of DU munitions dates back to the 1960s, with test programmes having been conducted at several Ministry of Defence (MoD) sites. The environmental fate of DU has, however, only recently begun to receive attention in the scientific literature, mostly in relation to areas such as the former Yugoslavia[7–14] and the Persian Gulf[15,16] where DU munitions have been used in active warfare. While such studies have successfully identified DU in numerous environmental samples collected from these regions of conflict, the investigative efforts were often hampered by the sporadic nature of the contamination and the associated difficulties of sampling in a former combat zone where the DU inputs are multidirectional, often occurring over a wide area, and the affected sites are highly disturbed. By contrast, the UK MoD testing sites, which have received little attention in the literature, provide an ideal opportunity to study the environmental fate of DU because each site has (i) a consistent firing direction with precisely recorded details of firing events, (ii) a known prevailing wind direction and (iii) relatively little post-firing disturbance to the immediate and surrounding area. Moreover, variation in soil type exists between sites, thus enabling investigation of DU fate in contrasting environmental settings. Therefore, investigations at these MoD sites have the potential to provide valuable information on DU and its ultimate fate in the environment that is relevant and transferable to the various active combat zones around the world where DU munitions have been used. Our goal in this investigation was to establish the extent of DU contamination in soil and biological materials at these sites arising from the munitions testing programme. Our combined use of alpha spectrometry and mass spectrometry for identifying and quantifying DU contamination in environmental

Table 1 Isotope abundances and activity ratios in natural and depleted uranium

	Atom abundance %			Mass ratio		Activity ratio	
	^{238}U	^{235}U	^{234}U	$^{235}U : {}^{238}U$	$^{234}U : {}^{238}U$	$^{235}U : {}^{238}U$	$^{234}U : {}^{238}U$
Natural U	99.27	0.72	0.0055	0.0072	0.000055	0.046	0.8–1.2[a]
DU	99.80	0.20	0.0009	0.0020	0.000009	0.013[b]	0.193

[a] Common activity ratio range observed in soils.[3,4] [b] DU values from ref. 6.

samples enabled us to accomplish an additional aim, that of examining the utility of the two techniques for such analyses.

Methods

Study sites

The two firing ranges used by the MoD for DU munitions research are the Dundrennan Firing Range, in Dumfries and Galloway, SW Scotland, and the Eskmeals Firing Range, in Cumbria, NW England (Fig. 1). Soils and biological (plant and earthworm) material were sampled at these ranges during June–August 2005. As outlined below, the sampling strategy was influenced by the specific weapons testing programmes conducted at each of the sites.

Historical perspective and sampling strategy

Dundrennan Firing Range. The test programme at the Dundrennan Firing Range began in 1982 and involved strength of design and firing accuracy trials for DU projectiles. The DU shells were fired from fixed positions into soft, hessian target screens mounted in gantries along the cliff-top facing the Solway Firth.[17] The projectiles were intended to pass through the screens unhindered and continue out to sea before striking the water several kilometres offshore.[17,18] Sampling focused around the two firing points where most of the testing on the range occurred, known as Raeberry and Balig Guns (Fig. 2 and 3; Table 2).

The Raeberry Gun firing position was used for the majority of the strength of design tests conducted on prototype DU ammunition. MoD records indicate that from an approximate 1800 firings, 71 malfunctions, where DU shells broke up when fired, occurred during testing.[17] It has already been shown that such malfunctions could potentially contaminate soils in the area surrounding the gun.[18] Samples were therefore collected at 12 sites around Raeberry Gun (Fig. 2; Table 2), including a site midway along the firing line near a small underground shelter (Raeberry Bunker) and a site in the vicinity of a nearby tank hulk (Raeberry Tank). Samples were also collected 1 m in front of and 1 m behind the base of the target (Raeberry Target A and B, respectively), because on rare occasions DU shells or shell fragments have struck target gantries resulting in possible DU contamination of surrounding soil. A control site (Raeberry Gun West) was selected on the basis that it was located upwind (prevailing wind direction is WSW to ENE) of the firing site, and therefore should have received little or no DU contamination.

The Balig Gun firing position was used for accuracy assessments, as opposed to projectile strength of design testing, thus far fewer firing malfunctions occurred at this site. It is estimated that only 15 malfunctions from a total of 1500 firings occurred here during the trials.[17] Although it was expected that the level of DU contamination would be far less at this location, samples were collected from nine sites around Balig Gun (Fig. 3; Table 2). Again, two samples were collected near the target (India Gantry). Due to the highly compacted and rocky nature of the ground immediately beneath and around the target, however, the samples were taken at approximately

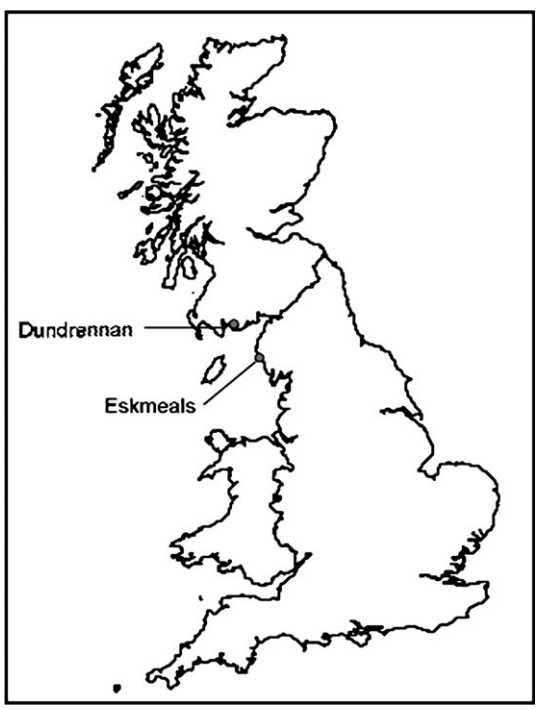

Fig. 1 Line map of Great Britain showing locations of Dundrennan (SW Scotland) and Eskmeals (NW England) Firing Ranges.

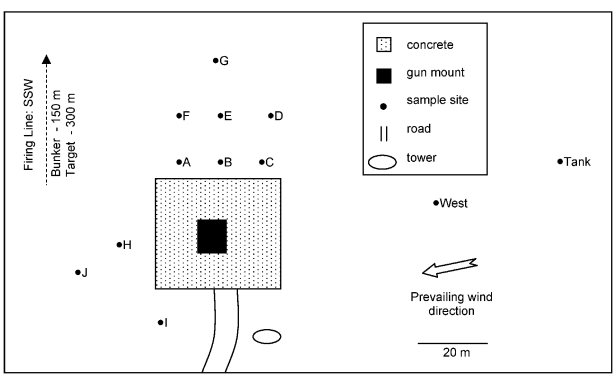

Fig. 2 Sampling pattern around Raeberry Gun, Dundrennan Firing Range, SW Scotland.

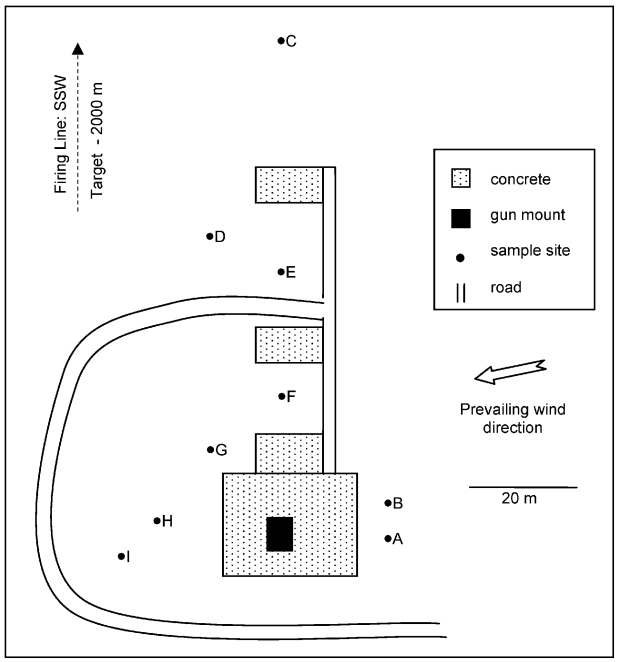

Fig. 3 Sampling pattern around Balig Gun, Dundrennan Firing Range, SW Scotland.

12 m (India Gantry A) and 15 m (India Gantry B) in front of the target.

Eskmeals Firing Range. At Eskmeals, testing of DU munitions began in the 1960s and continued until 1995, with the most intense period of research occurring during the 1980s.[18] The test programme involved firing DU projectiles at hard target arrays enclosed within a butt (designated VJ Butt). This type of testing potentially exposed the area immediately surrounding the butt to DU contamination from aerosols and DU fragments produced on impact. Because of this potential contamination, a radiation control zone (approximately 3 ha) around VJ Butt was established by the MoD as a precautionary measure. Soil and vegetation samples were collected at several sites within this zone, including three points (Pad Edge A–C) extending out from the edge of the concrete pad upon which the butt sits (Fig. 4, Table 2). This area was chosen because the soil and vegetation here were probably contaminated not only by DU aerosols and fragments produced from impacts, but also by washings of the concrete surface. Samples (Waste Storage A–B) were also taken from a site where armour plating (including DU armour) had been stored after impact testing with DU projectiles. A third site, at ~80–100 m to the NE of the firing position, but still within the radiation control zone, was sampled as a reference (Reference Point). It was expected that any DU contamination would be localised around the target and waste storage sites and that the Reference Point soil would therefore give an indication of near background levels of uranium.

Sample collection and processing

Soils. Following removal of the surface vegetation, soil samples were collected using a spade. Where possible, soils

Table 2 Locations of sampling sites at the Dundrennan and Eskmeals Firing Ranges

Sampling site	Co-ordinates	Relative position[a]	Sampling site	Co-ordinates	Relative position[a]
Dundrennan Firing Range			Dundrennan Firing Range		
Raeberry Gun	54°46′27.3″N, 004°00′51.9″W		Balig Gun	54°47′17.3″N, 004°00′12.7″W	
A–C	″	22 m in front	A–B	″	Upwind; W side of pad
D–F	″	26 m in front	C	54°47′11.8″N, 004°00′15.6″W	80 m in front
G	″	38 m in front	D–E	54°47′17.3″N, 004°00′12.7″W	~45 m in front
H–J	″	Downwind; E side/behind pad	F	″	20 m in front
West	54°46′27.9″N, 004°00′54.1″W	Upwind; ~55 m W of pad	G–I	″	Downwind; E side of pad
Bunker	54°46′21.9″N, 004°00′54.6″W	~150 m in front	India Gantry A–B	54°46′14.8″N, 004°00′40.4″W	2000 m in front
Tank	54°46′27.3″N, 004°00′56.5″W	Upwind; ~80 m W of pad			
Target A–B	54°46′18.9″N, 004°00′55.7″W	300 m in front			
Eskmeals Firing Range					
VJ Butt					
Pad Edge	54°19′25.2″N, 003°24′55.5″W	Downwind; S side of pad			
A	″	1 m from pad			
B	″	2 m from pad			
C	″	4 m from pad			
Waste Storage A–B	54°19′23.5″N, 003°24′50.6″W	Downwind; 50 m from pad			
Reference Point	54°19′26.9″N, 003°24′50.0″W	Upwind; 100 m NNE of pad			

[a] Distance from gun mount to end of concrete pad (along firing line) is 18 m at Raeberry Gun and ~15 m at Balig Gun.

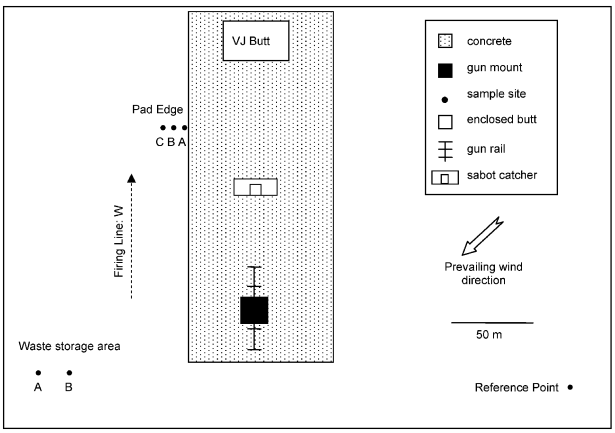

Fig. 4 Sampling pattern around VJ Butt, Eskmeals Firing Range, NW England (area shown is within the MoD radiation control zone).

were sampled to a depth of 10–15 cm. The soils at Raeberry Gun and India Gantry, however, were shallow and stony, hence samples from depths of less than 10 cm were collected at some sites around these locations. Between 2 and 3 kg (dry mass equivalent) of soil were collected at each site on the Dundrennan range, while 0.5–2 kg were collected at Eskmeals sites. Soil samples were sealed in plastic bags for transportation to the laboratory, where they were dried at 40 °C, ground to pass through a 2 mm sieve and stored in airtight containers. For radiometric measurements, subsamples (*ca.* 20 g) of each soil were dried at 105 °C.

Vegetation. The vegetation within the Dundrennan and Eskmeals Firing Ranges consists largely of mixed grasses (including *Festuca*, *Deschampsia* and *Molinia* species), rushes (*Juncus* sp.,) along with gorse (*Ulex europaeus*) and other woody shrubs.[19,20] The vegetation around Balig Gun (Dundrennan Firing Range) was an exception because this firing point was located in an area of improved grassland that was characteristically dominated by rye-grass (*Lolium* sp.) Above ground vegetation (mixed grass and rush species) was sampled at each site by cutting at approximately 3 cm above the soil surface. Plant material was placed in paper envelopes for transportation to the laboratory where it was washed with deionised water, dried at 70 °C for 48 h, cut up finely with scissors, and stored in airtight plastic containers.

Earthworms. Earthworms recovered from Raeberry Gun soil samples (prior to soil drying) were prepared for analysis in line with published methods,[11,21,22] whereby they were rinsed in deionised water to remove adherent soil particles and placed in empty plastic containers where they were kept for 3–4 days to allow them to purge the contents of their digestive systems. The earthworms were washed daily and placed in fresh containers to prevent re-ingestion of faecal matter. Any earthworms which had died during the purging period were removed. After the purging period, earthworms were frozen in a conventional freezer, snap frozen in liquid nitrogen, freeze dried and stored in sealed containers, and kept at 4 °C until analysis. The earthworms were of the species *Aporrectodea longa*, *A. caliginosa* and *Lumbricus terrestris*, which are the most prevalent in the area.[23]

Analytical methods

Soil characterisation. Soil pH was determined in 1 : 5 soil : water extracts ($n = 2$) using a Jenway pH electrode and combination meter (4330) following 2 h end-over-end shaking and 45 min standing time. Loss on ignition (450 °C for ≥ 6 h, $n = 2$) was used as a measure of soil organic matter content. Following treatment with H_2O_2 to remove organic material, soil particle size distribution (% sand, silt and clay) was determined using the hydrometer method.[24]

Uranium concentration analysis. Total soil U concentrations were determined *via* microwave-assisted digestion (CEM Mars 5) using an adapted version of the USEPA method 3052 (0.25 g soil + 9 mL HNO_3 + 1 mL HF; $n = 2$). The modification to the method entailed dry ashing samples in a muffle furnace (450 °C for ≥ 6 h) to remove organic material before digestion. The microwave operating details have been published elsewhere.[25] Filtered digest solutions (2% v/v Aristar HNO_3) were analysed by inductively coupled plasma–optical emission spectrometry (ICP–OES) using an Optima 5300 DV instrument (Perkin Elmer, UK) with a GemCone nebuliser and a Perkin Elmer autosampler (AS 93 plus). Total U concentrations in plant tissues were determined ($n = 3$) using the same method of digestion and analysis, but the significantly lower U concentrations in the plant tissues necessitated separate analysis by inductively coupled plasma–mass spectrometry (ICP–MS) using a PlasmaQuad (PQ) 3 instrument (VG Elemental, Winsford, UK) with a nickel sampler and skimmer cones, a Meinhard nebulizer, a Gilson autosampler and a Gilson Minipuls 3 peristaltic pump (Anachem, Luton, UK).

Uranium isotope analysis. The activities of ^{234}U, ^{235}U and ^{238}U in soil samples were determined by alpha spectrometry. The method employed is consistent with others reported in the literature.[4,13,26,27] Soil samples (2 g, $n = 3$) were ashed at 600 °C for 6 h or more to vaporise organic components. Once cooled, ashed samples were spiked with ~1 Bq ^{232}U as a yield tracer, with 5 mL 9 M HCl also added to aid tracer–sample equilibration. Next, samples were acid digested in a hot 1 : 1 HCl : HNO_3 mixture for 6 h, evaporated to near dryness and treated with H_2O_2 to remove any remaining organics. Residues were evaporated again and further digested with concentrated HF for 8 h, after which they were evaporated once more before being re-dissolved in 4 M HNO_3. The U and Th present in the sample solutions were co-precipitated with $Fe(OH)_3$ by adding ammonia solution (35%, added as supplied) with the precipitate then separated from solution by centrifugation and decanting. Precipitates were rinsed with deionised water, re-centrifuged and dissolved in concentrated HCl. Samples were then evaporated to near dryness, dissolved in 9 M HCl and subjected to solvent extraction with di-isopropyl ether to remove Fe. Following this, sample solutions were passed through glass columns containing chloride form anion exchange resin (Bio-Rad, AG1-x8, 100–200 mesh, pre-conditioned with ~20 mL 1.2 M HCl followed by ~20 mL 9 M HCl) for U–Th separation. After rinsing with 2 × 25 mL 9 M HCl to ensure all Th had been flushed, U adhering to the resin was eluted with 150 mL 1.2 M HCl. The eluted samples were then evaporated to near dryness and taken up in 3.75%

(w/v) NH_4Cl solution, from which the U present was electrodeposited onto stainless steel planchettes (2 h electrodeposition time) for counting by alpha spectrometry (silicon surface barrier detector, Octête plus, Ortec, USA). The counting time varied (3–21 days) depending on sample activity. In addition to determination of isotope activities and activity ratios, the fraction of U in the samples attributable to DU (fDU) was computed using a mixing ratio calculation, where the sample U isotope activity ratio ($^{235}U : {}^{238}U$) was treated as a function of the isotope ratios of natural and depleted U:

$$^{235}U : {}^{238}U = 0.013 f\mathrm{DU} + 0.046(1 - f\mathrm{DU})$$

$$\therefore f\mathrm{DU} = \frac{0.046 - {}^{235}U : {}^{238}U}{0.033}$$

where $^{235}U : {}^{238}U$ is the isotope activity ratio of the sample, 0.013 the activity ratio in DU and 0.046 the activity ratio in natural U.

Accuracy and precision of the isotopic measurements were tested using International Atomic Energy Association certified reference soil IAEA-326, having certified specific activity values for ^{234}U and ^{238}U, with the results being within the stated uncertainties for the certified values (Table 3). Uranium isotope distribution in plant and earthworm tissues was determined by multi-collector inductively coupled plasma–mass spectrometry (MC–ICP–MS, upgraded Micromass IsoProbe, GV Instruments, UK) analysis of digest solutions produced *via* the microwave digestion method described above (additional digests were carried out for the plant samples using masses of 0.2–0.7 g, depending on plant tissue U concentration, *i.e.* isotopic analysis was not performed on the solutions analysed for total U). The masses digested for earthworm samples were in the range 200–400 mg freeze dried material. The chemical separation procedures used to isolate U in these digest solutions and the MC–ICP–MS instrument settings and techniques employed have been described elsewhere.[28] MC–ICP–MS was utilised for these analyses because the U concentrations in plant and earthworm samples were anticipated to be too low for isotope quantification using the alpha spectrometry method employed for the soil samples. Consequently, fDU values for earthworm and plant samples were calculated using a mixing ratio employing $^{235}U : {}^{238}U$ isotope mass ratios rather than activities (adapted from ref. 12 and 29):

$$^{235}U : {}^{238}U = \frac{0.72(1 - f\mathrm{DU}) + 0.2 f\mathrm{DU}}{99.27(1 - f\mathrm{DU}) + 99.80 f\mathrm{DU}}$$

$$\therefore f\mathrm{DU} = \frac{0.72 - 99.27\,{}^{235}U : {}^{238}U}{0.52 + 0.53\,{}^{235}U : {}^{238}U}$$

where $^{235}U : {}^{238}U$ is the isotope mass ratio of the sample; 0.72 the mass abundance % of ^{235}U in natural U and 0.2 the corresponding value in DU; 99.27 is the mass abundance % of ^{238}U in natural U and 99.80 the corresponding value in DU.

Results and discussion

Soil characterisation

Soil particle size distribution was consistent across all samples from the Dundrennan Firing Range, with values that would identify the soils as clay loams or sandy clay loams (40–55% sand, 20–25% silt, 22–32% clay). Contrastingly, the soils at the Eskmeals Firing Range were sands (~100% sand). The organic matter (OM) content of the soils differed considerably, both amongst the Dundrennan soils (7–18% OM) and between those and the soils from Eskmeals (~2%, except at the Reference Point which recorded 8% OM). The Dundrennan samples were relatively uniform in terms of pH (~5.5–6.0), with the exception of Raeberry Gun H which had a value 1–2 units above those of neighbouring sites (pH 7.4). A possible explanation for this elevated pH is the accumulation of leachates (*e.g.* $Ca(OH)_2$) downslope of the concrete pad. Eskmeals soils were rather varied in terms of pH, recording values across the range of 5.6–7.8.

DU contamination of soils at the Dundrennan Firing Range

Raeberry Gun soil samples (A–F, H) showed consistent DU contamination in the immediate vicinity of the firing position (Table 3), with U concentrations in the range of 20–38 mg kg^{-1} and isotope activity ratios often approaching that of DU itself (~0.013 for $^{235}U : {}^{238}U$, Fig. 5). Accordingly, the fDU values for these soils were in the range of 85–100%, indicating that DU was overwhelmingly the greatest source of U in these soils. Contamination levels decreased with distance along the firing line, with Raeberry Gun G site (approximately 38 m from the firing position) having a soil U concentration of 7.5 mg kg^{-1} and an isotope ratio reflecting a mix of both DU (~75%) and natural U. At a distance of 150 m, the Raeberry Bunker soil had an isotopic signature statistically indistinguishable from natural U. Similarly, based on isotope activity ratios, the upwind sites to the west of Raeberry Gun (sites West and Tank) showed no evidence of DU contamination, while sites I and J revealed that significant DU contamination was present both behind and on the downwind side of the firing position. For Balig Gun samples, soil U concentrations were lower (1.7 to 14 mg kg^{-1}), with isotope activity ratios and, consequently, fDU values indicating much less DU present. Similar to Raeberry Gun, the amount of DU soil contamination decreased with distance along the firing line, with Balig Gun C, at ~60 m from the firing point, having a soil $^{235}U : {}^{238}U$ activity ratio approaching that of natural U. Balig Gun A and B indicated the presence of DU in the soil immediately to the upwind side of the firing pad (fDU 20 and 23%, respectively), but much less than at the corresponding site on the downwind side (site H, fDU 55%). As was the case with Raeberry Target, the soil around India Gantry (the target for Balig Gun) was also contaminated, indicating that unintentional DU penetrator impacts against gantry frames had led to DU dispersal around target bases.

DU contamination of soils at the Eskmeals Firing Range

The U concentrations in samples from within the radiation control zone enclosing VJ Butt were typically higher than

Table 3 U concentration (mg kg^{-1}, ± std deviation, $n = 2$), isotope activity ratios (± uncertainty[a], $n = 3$), total U specific activity (Bq kg^{-1}, ± uncertainty[a], $n = 3$) and fraction DU (*f*DU, as %) in soil samples from Dundrennan and Eskmeals Firing Ranges. N/A: not applicable

Site	U/mg kg^{-1}	Total U specific activity/ Bq kg^{-1}	^{235}U : ^{238}U	^{234}U : ^{238}U	*f*DU (%)	Site	U/mg kg^{-1}	Total U specific activity/ Bq kg^{-1}	^{235}U : ^{238}U	^{234}U : ^{238}U	*f*DU (%)
Dundrennan						Dundrennan					
Raeberry Gun						Balig Gun					
A	37.7 ± 2.4	861 ± 5.8	0.0119 ± 0.0004	0.165 ± 0.0023	102	A	3.6 ± 0.6	61 ± 0.6	0.040 ± 0.0026	0.92 ± 0.0195	20
B	20.4 ± 2.1	536 ± 3.8	0.0166 ± 0.0007	0.193 ± 0.0030	88	B	3.2 ± 0.4	57 ± 0.6	0.038 ± 0.0024	0.87 ± 0.0179	23
C	33.4 ± 1.1	793 ± 5.5	0.0133 ± 0.0005	0.162 ± 0.0025	98	C	2.6	55 ± 0.6	0.043 ± 0.0028	0.92 ± 0.0196	8
D	32.7 ± 1.3	690 ± 4.0	0.0120 ± 0.0004	0.171 ± 0.0021	102	D	3.3 ± 0.8	56 ± 0.6	0.045 ± 0.0025	0.84 ± 0.0183	4
E	32.4 ± 1.7	807 ± 4.4	0.0122 ± 0.0003	0.170 ± 0.0019	101	E	3.4	28 ± 0.3	0.037 ± 0.0022	0.76 ± 0.0144	29
F	25.9 ± 1.1	532 ± 4.1	0.0145 ± 0.0006	0.174 ± 0.0027	95	F	6.6 ± 0.2	106 ± 1.0	0.023 ± 0.0014	0.44 ± 0.0086	70
G	7.5[b]	146 ± 1.1	0.0211 ± 0.0011	0.382 ± 0.0060	75	G	14.0 ± 0.7	260 ± 1.7	0.014 ± 0.0005	0.24 ± 0.0033	96
H	25.1 ± 17.3	329 ± 2.5	0.0134 ± 0.0006	0.215 ± 0.0034	98	H	4.9 ± 0.2	50 ± 0.5	0.028 ± 0.0017	0.54 ± 0.0109	55
I	1.8 ± 0.6	57 ± 0.7	0.0343 ± 0.0029	0.903 ± 0.0215	35	I	1.7 ± 0.4	71 ± 1.1	0.041 ± 0.0031	0.83 ± 0.0204	15
J	7.2	79 ± 0.6	0.0268 ± 0.0014	0.542 ± 0.0072	58	India Gantry A	11.7 ± 4.7	134 ± 1.0	0.019 ± 0.0009	0.36 ± 0.0055	82
West	0.8 ± 0.6	50 ± 0.4	0.0451 ± 0.0021	0.942 ± 0.0153	3	B	6.4 ± 0.6	57 ± 0.6	0.030 ± 0.0022	0.73 ± 0.0164	47
Tank	3.7 ± 0.4	51 ± 0.7	0.0441 ± 0.0037	0.916 ± 0.0256	0						
Bunker	1.6 ± 0.9	63 ± 0.7	0.0417 ± 0.0030	0.912 ± 0.0282	0						
Target A	4.7 ± 0.3	92 ± 0.7	0.0310 ± 0.0017	0.651 ± 0.0116	45						
Target B	2.6 ± 0.3	75 ± 0.7	0.0276 ± 0.0017	0.530 ± 0.0106	55						
Eskmeals						Reference soil (IAEA soil 326)					
VJ Butt						Measured	3.2 ± 1.5	50 ± 0.4	0.046 ± 0.0024	0.88 ± 0.016	0
Pad Edge A	282 ± 142	5925 ± 4.7	0.0142 ± 0.0003	0.157 ± 0.0022	96	Certified	2.36	N/A	N/A	0.87 ± 0.080	N/A
Pad Edge B	62	919 ± 6.2	0.0142 ± 0.0003	0.167 ± 0.0020	95						
Pad Edge C	21 ± 0.6	436 ± 4.1	0.0135 ± 0.0007	0.208 ± 0.0040	98						
Waste Storage A	18 671 ± 3346	268 836 ± 10 391	0.0151 ± 0.0010	0.193 ± 0.0124	93						
B	68 ± 2.5	1311 ± 10	0.0151 ± 0.0005	0.153 ± 0.0022	93						
Reference point	4.0 ± 0.4	66 ± 0.7	0.0187 ± 0.0014	0.283 ± 0.0067	82						

[a] The reported ± uncertainty values encompass uncertainties associated with tracer activity (^{232}U), counting statistics (tracer and test nuclides), sample weighing and sample replication. [b] Single replicate analysed for total U concentration of this sample, thus no standard deviation.

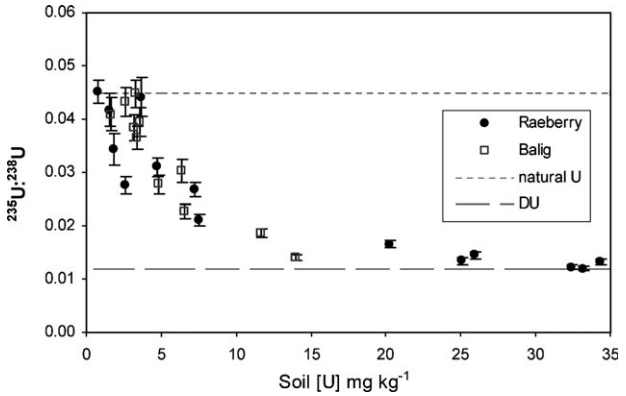

Fig. 5 Soil U concentration *vs.* ^{235}U : ^{238}U isotope activity ratio for Raeberry and Balig Gun soil samples. Natural and DU isotope ratio lines indicated. Error bars, where they exceed symbol margins, show uncertainties associated with tracer activity (^{232}U), counting statistics, sample weighing and sample replication.

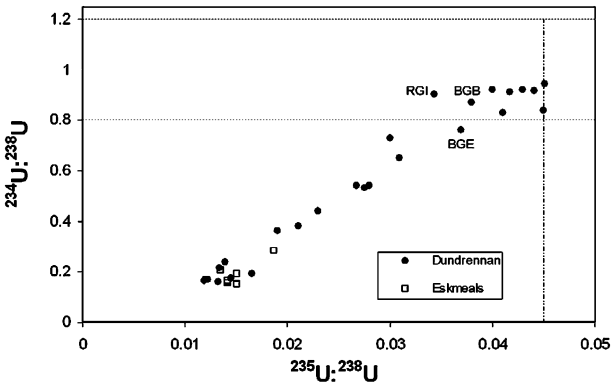

Fig. 6 ^{235}U : ^{238}U *vs.* ^{234}U : ^{238}U ratios for Dundrennan and Eskmeals soils. The horizontal dashed lines indicate the range (upper and lower limits) of the ^{234}U : ^{238}U ratio observed for natural U in soils, thus values below are indicative of DU affected soils. The vertical dashed line indicates the natural ^{235}U : ^{238}U ratio, thus all values to the left identify soils as DU affected. Samples Balig Gun B (BGB), Raeberry Gun I (RGI) and Balig Gun E (BGE) are indicated.

those from the Dundrennan Firing Range. Particularly elevated ($>18\,000$ mg kg^{-1}) concentrations were observed for the Waste Storage A sample. The isotope activity ratios (*f*DU in the range 93–98% for Pad Edge and Waste Storage sites, Table 3) confirmed that the uranium in these soils was predominantly DU. The Reference Point, at some distance behind the firing position, also had a soil U concentration in excess of what might be expected for a non-contaminated sandy soil (*i.e.* 1–2 mg kg^{-1}) and had a U isotopic signature indicative of considerable DU contamination (*f*DU calculated at 82%).

In the wider context, it is worth noting that the U concentrations and isotope activity ratios of some of the soils examined here (both sites) are comparable to those reported for areas of Kosovo subjected to heavy attacks with DU ammunition during the 1999 conflict,[9,11,14,30] indicating a similar degree of contamination. In those Kosovo studies, the highest soil U concentrations and activities were observed in areas where penetrator impacts against hard targets had caused dispersal of DU aerosols, which is a finding consistent with that of the present study.

Utility of $^{234:238}U$ *vs.* $^{235:238}U$ isotope activity ratios for determining soil DU contamination

While both the ^{234}U : ^{238}U and ^{235}U : ^{238}U ratios can be used to examine DU contamination in the environment, our results demonstrate the greater precision with which contaminated sites can be identified using the ^{235}U : ^{238}U ratio (Fig. 6). That is, because only a range for natural ^{234}U : ^{238}U activity ratios can be stated rather than a specific value, as is the case with ^{235}U : ^{238}U, soils may need to be considerably contaminated before their ^{234}U : ^{238}U ratio falls below this range and identifies them as DU-affected. This can clearly be seen in Fig. 6, which shows that several soil samples that fell within the natural ^{234}U : ^{238}U ratio range were identified as contaminated using the more precise ^{235}U : ^{238}U method. For example, Balig Gun B and Raeberry Gun I, having *f*DU values of 23% and 35%, respectively (Table 3), fall within the natural range for ^{234}U : ^{238}U, and thus would not have been identified as contaminated using this ratio. Furthermore, Balig Gun E would be the least contaminated soil identified as DU-affected using ^{234}U : ^{238}U (Fig. 6), but was revealed to have an *f*DU of 29% using the mixing ratio calculation based on ^{235}U : ^{238}U (Table 3). These results agree with the findings of Magnoni *et al.*,[29] who concluded that DU contamination was only identifiable using the ^{234}U : ^{238}U ratio when the composition was about 20% DU or greater. Therefore, our results demonstrate that the ^{235}U : ^{238}U ratio is far superior for accurately determining the extent of soil DU contamination.

Plant uptake of DU at the Dundrennan and Eskmeals Firing Ranges

Plant U concentrations were highest in the samples from within the VJ Butt control zone (Table 4), with site Waste Storage B having the maximum concentration observed (3.38 mg kg^{-1}). This site also exhibited by far the highest plant concentration : soil concentration ratio (CR = 0.05). However, while plant tissue U concentrations were related to soil concentrations (R^2 = 0.51 for Raeberry Gun and 0.43 for Balig Gun samples) the relationship was not linear (Fig. 7), which is in agreement with numerous studies investigating plant assimilation of U.[31–33] Isotope mass ratios in plant samples revealed DU had been assimilated by plants growing on contaminated soils at all locations (Table 4). Raeberry Gun and VJ Butt area plant samples had isotope mass ratios approaching that of DU itself, reflecting the respective soil isotopic signatures, while the Balig Gun sample presented a mixed DU–natural U signature. This result is not surprising, considering the lower level of contamination in the soils surrounding Balig Gun. These results agree with other findings reported in the literature where non-natural U in soils has been transferred to plant tissues.[34,35] The results presented here also demonstrate the utility of MC–ICP–MS for such measurements, as to perform the U isotope measurements for Raeberry Gun plant samples using alpha spectrometry would have required sample sizes of 45–100 g per replicate in order to obtain sufficient counts ($\sim$500) to quantify ^{235}U activity

Table 4 Uranium concentrations (μg kg^{-1}, ± std deviation, $n = 3$), plant : soil U concentration ratios (×1000),[a] isotope mass abundance ratios (selected samples, ± relative error as %) and fraction DU (*f*DU, as %) for above ground plant tissues from sampling sites at the Dundrennan and Eskmeals Firing Ranges

Site	U	CR[a] (×1000)	^{235}U : ^{238}U	^{234}U : ^{238}U	*f*DU (%)
Dundrennan					
Raeberry Gun					
A	30 ± 7.4	1.02	0.00263 ± 9.83%	0.0000251 ± 3.41%	88
B	8 ± 0.7	0.40			
C	[b]	—			
D	25 ± 4.2	0.76	0.00248 ± 1.56%	0.0000107 ± 0.90%	91
E	8 ± 2.7	0.26			
F	14 ± 4.3	0.56	0.00265 ± 2.01%	0.0000163 ± 1.36%	88
G	14 ± 6.0	1.85	0.00266 ± 0.46%	0.0000131 ± 0.56%	88
H	18 ± 4.1	0.71	0.00297 ± 0.79%	0.0000171 ± 0.65%	82
I	7 ± 0.4	4.06			
J	9 ± 0.7	1.18			
West	7 ± 4.2	8.94			
Tank	[b]	—			
Bunker	6 ± 1.2	3.64			
Target A	4 ± 1.3	0.91			
Target B	4 ± 1.0	2.42			
Balig Gun					
A	6 ± 1.4	1.69			
B	10 ± 6.7	3.00			
C	5 ± 2.7	1.92			
D	4 ± 1.7	1.32			
E	4 ± 1.0	1.26			
F	3 ± 0.4	0.43			
G	12 ± 3.6	0.83	0.00440 ± 2.71%	0.0000270 ± 1.49%	55
H	6 ± 2.7	3.88			
I	10 ± 2.5	0.86			
India Gantry A	7 ± 1.1	1.09	0.00274 ± 1.87%	0.0000167 ± 1.26%	86
India Gantry B	6 ± 1.4	1.69			
Eskmeals					
Pad Edge A	1020 ± 17	3.62	0.00212 ± 0.05%	0.0000083 ± 0.23%	98
B	112 ± 66	5.46	0.00212 ± 0.03%	0.0000081 ± 0.12%	98
C	440 ± 279	7.10	0.00224 ± 0.18%	0.0000096 ± 0.25%	96
Waste Storage A	1270 ± 265	0.08			
B	3378 ± 1054	49.97	0.00227 ± 0.02%	0.0000104 ± 0.15%	95
Reference Point	[b]	—			

[a] The CR values reported in the table have been multiplied by 1000 for ease of viewing. [b] Scandium detected in digest solution indicating contamination of sample with soil particles, therefore value not reported.

confidently within a 3 week counting period. Therefore, while alpha spectrometry remains a highly useful tool for examining environmental samples with U concentrations at or above the range observed in soils, MC–ICP–MS is a more suitable technique for analysing samples with lower U concentrations (*e.g.* plant, earthworm or water samples) or when sample size is limited.

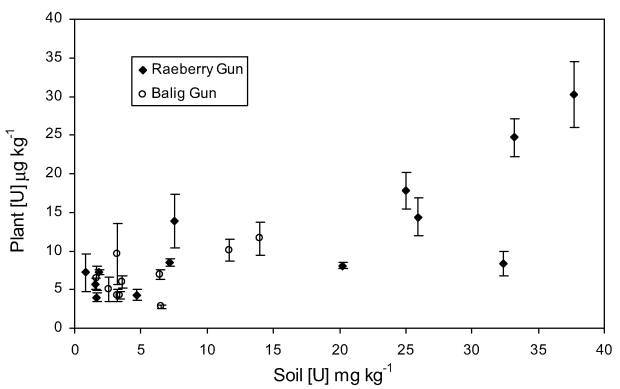

Fig. 7 Above ground plant tissue U concentrations (μg kg^{-1}) *vs.* soil U concentrations (mg kg^{-1}) for Raeberry Gun (closed symbols) and Balig Gun (open symbols) samples. Error bars, where they exceed symbol margins, show standard error about means.

DU uptake by earthworms at the Dundrennan Firing Range

Earthworms collected from Raeberry Gun soil samples also displayed isotope mass ratios strongly affected by DU (Table 5), again reflecting soil U concentration and isotopic composition. This contrasts with the results of Di Lella *et al.*,[11] who found U in the tissues of earthworms living in DU ammunition-bombarded soils of Kosovo to be largely of natural composition. The conflicting results may have arisen due to the soils from around Raeberry Gun (from which we collected earthworms) having a more consistent level of DU

Table 5 Uranium isotope mass ratios (± relative error, as %) and fraction DU (*f*DU, as %) in earthworm tissues

Collection site	^{235}U : ^{238}U	^{234}U : ^{238}U	*f*DU (%)
Raeberry Gun B	0.00210 ± 0.1%	0.0000071 ± 0.4%	99
Raeberry Gun C	0.00212 ± 0.1%	0.0000073 ± 0.4%	98
Raeberry Gun F	0.00222 ± 0.1%	0.0000082 ± 0.3%	96
Raeberry Gun H	0.00228 ± 1.7%	0.0000008 ± 15.9%	95

contamination compared with the soils investigated in the Kosovo study, which were very heterogeneous in this respect.

Conclusions

Many of the soil samples from the Dundrennan Firing Range and all soils examined from within the VJ Butt control zone at the Eskmeals Firing Range had U concentrations and isotopic signatures indicative of contamination with DU. Within the Dundrennan Firing Range, DU contamination was largely localised around the firing positions and target gantries (particularly for the Raeberry Gun firing point), with contamination decreasing with distance along the firing line and in the direction of the prevailing wind. Of all the soils examined, the highest contamination observed was at the Waste Storage Area within the VJ Butt control zone, where U concentrations exceeded 18 000 mg kg^{-1}. Since soil characterisation showed that there were differences in pH, texture and organic matter content (i) between the soils from the two ranges and (ii) among soils within each range, albeit more subtle, there may be differing soil–U associations which will strongly influence the mobility and environmental fate of DU. Furthermore, plants and earthworms collected from above and within contaminated soils, respectively, also had U isotopic signatures strongly influenced by DU, indicating that DU was indeed assimilated into biological tissues. This emphasises the need for detailed characterisation of U associations in soil and, importantly, the soil pore waters to determine DU bioavailability and mobility in these environments. Finally, this study has demonstrated the continued appropriateness of alpha spectrometry for quantifying the extent of DU contamination in soils, with the ^{235}U : ^{238}U activity ratio being a far more precise tool than ^{234}U : ^{238}U, while MC–ICP–MS was demonstrated as the more suitable technique for assessing environmental samples with low U concentrations (*e.g.* biological samples). This observation has significance because alpha spectrometry instrumentation is far less expensive than MC–ICP–MS and is consequently more widely available.

Acknowledgements

This investigation would not have been possible without the support of the Natural Environment Research Council (NERC, grant NE/C513134/1) and the cooperation of the UK MoD. The authors also thank Mr J. Hackett (Head Ranger, Dundrennan), Mr T. Geer (Radiation Adviser, QinetiQ) and Mrs C. Toqué (DSTL) for their kind assistance.

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